**Topological analysis of zeolite-like compounds with mixed frameworks and crystal structure prediction using the approach of OD ("order-disorder") theory**

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Compounds with the general formula $Cs\{^{[6]}Al_2[^{[4]}TP_6O_{20}]\}$ (where $T$ = B [1], Al [2]) are based on microporous heteropolyhedral frameworks formed by tetrahedral borophosphate or aluminophosphate $[TP_6O_{20}]$-layers linked by isolated $AlO_6$ octahedra. The large framework cavities are filled by $Cs^+$ cations. As it was previously shown, both $Cs\{Al_2[BP_6O_{20}]\}$ and $Cs\{Al_2[AlP_6O_{20}]\}$ are of modular character [3] and can be considered as polytypes [1,4].

The symmetrical relations between the compounds have been analyzed using the OD theoretical approach [3,5,6] for the OD families containing more than one ($M$ > 1) kinds of layers [7]. The OD layers have been chosen in accordance with the equivalent region (ER) requirements [8]. Topological analysis of the frameworks was performed by means of natural tilings (the smallest polyhedral cationic clusters that form a framework) of the 3D cation nets [9] calculated using the ToposPro software [10].

The crystal structures of compounds with the general formula $Cs\{^{[6]}Al_2[^{[4]}TP_6O_{20}]\}$ (where $T$ = Al, B) display order-disorder (OD) character and can be described using the same OD groupoid family [11]. Their structures built up by two kinds of non-polar layers, with the layer symmetries $Pc(n)2$ ($L_{2n+1}$-type) and $Pc(a)m$ ($L_{2n}$-type) (category IV [7]). Layers of both types ($L_{2n}$ and $L_{2n+1}$) alternate along the **b** direction and have common translation vectors **a** and **c** ($a$ ~ 10.0 Å, $c$ ~ 12.0 Å). All ordered polytypes as well as disordered structures can be obtained using the following partial symmetry operators that may be active in the $L_{2n}$ type layer: the $2_1$ screw axis parallel to **c** [– – $2_1$] or inversion centers and the $2_1$ screw axis parallel to **a** [$2_1$ - -]. The symmetry relation common to all polytypes of this family are described by the OD groupoid family symbol:

$$\begin{matrix} Pc(n)2 \\ [r,0] \end{matrix} \qquad P\ 2_1/c\ (2/a)\ 2_1/m, \tag{1}$$

where $r$ = 0; the first line contains the layer-group symbols of the two constituting layers, while the second line indicates positional relations between the adjacent layers [12].

Different sequences of operators active in the $L_{2n}$ type layer ([– – $2_1$] screw axes or inversion centers and [$2_1$ – –] screw axes) define the formation of multilayered structures with the increased $b$ parameter, which are considered as non-MDO polytypes.

Compounds with the general formula $Rb\{^{[6]}M^{3+}[^{[4]}T^{3+}P_6O_{20}]\}$ ($M$ = Al, Ga; $T$ = Al, Ga) are based on heteropolyhedral $MT$-frameworks with the same stoichiometry as in $Cs\{^{[6]}Al_2[^{[4]}TP_6O_{20}]\}$ (where $T$ = Al, B). It was found that all the frameworks have common natural tilings, which indicates the close relationships of the two families of compounds.

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